

Chemical Modification of Fibers by the Graft Copolymerization of Reactive Monomers. (II)

Graft Copolymerization of Acrylic Acid onto Polypropylene and Polyvinyl Chloride Fibers*

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Some properties of polypropylene and polyvinyl chloride fibers grafted with acrylic acid using Co^{60} γ -ray irradiation method and aftertreated by use of the reactivity of acrylic acid units in the grafted side chains were examined.

Though the tensile properties of the grafted and aftertreated fibers were nearly equal to the original fiber, heat shrinkage of the fibers was remarkably decreased by the acrylic acid grafting and aftertreatment with inorganic metal salts. Tensile properties at elevated temperatures were not improved so much as expected from the decrease of heat shrinkability.

By the acrylic acid grafting and Na salt after treatment, moisture regain was increased and frictional electricity was remarkably decreased, while wet tensile strength, heat settability and dimensional stability in wet state were almost unchanged.

INTRODUCTION

Though synthetic fibers generally have many desirable characteristics, scanty of hydrophilic property is a shortcoming for some uses and some difficulties happen to its dyeability or frictional electricity. The fibers having moderate hydrophilic property and heat settability and holding original excellent mechanical properties even in wet state should be pursued as an aspect of ideal fiber.

Some synthetic fibers have relatively low melting or softening point and their practical uses are subjected to some restrictions. Improvement of heat stability of such synthetic fibers is an important problem. In relation to these problems, E. E. Magat *et al.*¹⁾ recently reported that increased moisture regain, high wet crease recovery, low electrical resistance and high melting temperature of nylon were obtained by acrylic acid grafting following by aftertreatment in aqueous solutions of some metallic salts.

Hitherto we have been engaged in chemical modification of hydrophilic fibers such as cellulose and polyvinyl alcohol by the graft copolymerization, but next we started the research of the graft copolymerization onto some hydrophobic fibers from the viewpoint above mentioned, and at first the interesting method

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developed on nylon by E. E. Magat *et al.*¹⁾ was applied to polypropylene and polyvinyl chloride fibers in order to examine in detail the effect of the treatment on the fiber properties. Tensile properties at elevated temperature or in wet state are important items to be examined.

EXPERIMENTAL

1. Materials

Polypropylene (PP) fiber : About 50 d/25 fil. multifilament yarn and about 400 d monofilament presented from Asahi Kasei Co. and Asahi Dow Co., were used after benzene extraction. Fabric presented from Asahi Kasei Co. was treated with 0.1% soap solution at 50°C, washed with water and dried in vacuum before use.

Polyvinyl chloride (PVC) fiber : About 275 d/60 fil. multifilament yarn manufactured by Teijin Co. (Teviron) was used after ether extraction.

Acrylic acid : Distilled in vacuum as usual.

tris(1-aziridinyl) phosphine oxide(APO) : Received as 50% benzene solution.

Zn(BF₄)₂ : Received as 45% aqueous solution.

Inorganic metal salts and organic solvents : Reagent grade.

2. Graft copolymerization

2.1. Polypropylene fiber and fabric

After pre-irradiation of Co⁶⁰ γ -ray under vacuum, acrylic acid aqueous solution in the case of the multifilament yarn and fabric, and benzene solution in the case of monofilament were added and heat polymerized under vacuum of 10⁻⁴ mmHg. The homopolymer was removed by washing with tap water. Ratio of the weight increase after drying under vacuum to the weight of the original sample was assumed to be % grafting.

2.2. Polyvinyl chloride fiber

Table 1. Aftertreatment of grafted fibers.

Aftertreatment with	Polypropylene multifilament yarn and fabric	Polypropylene monofilament	Polyvinyl chloride multifilament yarn
Na ₂ CO ₃	1% aqueous solution 60°C, 1 hr	5% aqueous solution 80°C, 1 hr	1% aqueous solution 50°C, 1 hr
Ca(CH ₃ COO) ₂	1% aqueous solution 60°C, 1 hr after treated with Na ₂ CO ₃	5% aqueous solution 80°C, 1 hr after treated with Na ₂ CO ₃	1% aqueous solution 50°C, 1 hr after treated with Na ₂ CO ₃
NH ₄ Cl	5% aqueous solution 60°C, 1 hr and cured at 140~145°C, 15 min		5% aqueous solution 50°C, 1 hr and cured at 125°C, 15 min
APO	50% APO benzene solution 50 part, water 43.3 part, nonionic emulsifier 1 part, 45% Zn(BF ₄) ₂ aqueous solution 5.7 part ; 60°C, 1 hr ; dried at 80°C, 5 min and cured at 130°C, 10 min		50% APO benzene solu- tion 33.4 part, water 62.2 part, nonionic emulsifier 1 part, 45% Zn(BF ₄) ₂ aqueous solu- tion 3.4 part ; 50°C, 1 hr ; dried at 80°C, 5 min and cured at 125°C, 15 min

Both methods of simultaneous and pre-irradiation were used for grafting. Acrylic acid used was diluted with organic solvent having affinity to PVC fiber. Removal of the homopolymer and calculation of % grafting were as same as described above.

2.3. Aftertreatment of the grafted fiber or fabric

The grafted fibers or fabrics were treated with inorganic metal salt aqueous solutions and APO as tabulated in Table 1.

2.4. Heat shrinkability

The fiber was heated at the rate of 2°C/min under the tension of 0.01 g/d and the change of its length with temperature was measured by cathetometer.

2.5. Fiber melting temperature

Fiber melting temperature was determined by placing fiber sample in an electrically heated tube and observing the temperature where the fiber broke under a slight load.

2.6. Frictional electricity

Rotary drum type static tester²⁾ developed in our laboratory was used at 20°C, 65% RH. Fiber sample was fixed on the drum and rubbed against a scoured nylon fabric which was stretched tight under the load of about 765 g. Size of sample was 40 mm length in the case of monofilament and 40×10 mm of fabric. The number of revolution of the drum was about 800 rpm.

2.7. Moisture regain

The sample dried at 40°C under vacuum was kept at 20°C, 65% RH for 50 hrs and the weight increase was determined.

RESULT AND DISCUSSION

1. Graft copolymerization of acrylic acid onto polypropylene fiber

Torikai *et al.*³⁾ have reported about graft copolymerization of acrylic acid onto PP fiber using electron beam pre-irradiation method by van de Graaff generator. Following them, acrylic acid grafted PP fiber was prepared by Co⁶⁰ γ -ray pre-irradiation method.

Percent grafting varied with the room temperature when the fiber was irradiated even if the same total dose was applied. Lower grafting % and more acrylic acid homopolymer were obtained at higher room temperature. As shown in Table 2~4, graft copolymer was obtained easily in each case of multifilament yarn, monofilament and fabric.

2. Graft copolymerization of acrylic acid onto polyvinyl chloride fiber

When aqueous solution of acrylic acid was used, only acrylic acid homopolymer was produced without any graft copolymer in either case of pre-irradiation or simultaneous irradiation. So the graft copolymerization was carried out using some organic solvents or swelling agents for PVC fiber and both methods of pre-

Table 2. Examples of graft copolymerization of acrylic acid onto polypropylene multifilament yarn.

Total dose 4.8×10^5 r; Dose rate 3.19×10^4 r/h;
 Fiber/monomer aqueous solution *ca.* 0.3 g/20 g;
 Polymerization temperature 60°C.

Pre-irradiation temperature (°C)	Concentration of acrylic acid aqueous solution (%)	Time of polymerization (hr)	% Grafting
20~25	10.0	3.0	4.4
"	20.0	"	14.8
"	30.0	"	25.3
"	"	"	29.5
"	40.0	"	40.7
5~10	5.0	4.0	38.2
"	10.0	"	110.0
"	5.0	2.0	28.2
"	"	2.5	26.4
"	"	3.0	36.5

Table 3. Examples of graft copolymerization of acrylic acid onto polypropylene monofilament.

Total dose 5.0×10^5 r; Dose rate 3.19×10^4 r/h;
 Fiber/monomer benzene solution *ca.* 0.2 g/20 g;
 Polymerization temperature 80°C.

Pre-irradiation temperature (°C)	Concentration of acrylic acid benzene solution (%)	Time of polymerization (hr)	% Grafting
20~25	60.0	5.0	43.3
"	65.0	"	18.6
"	70.0	"	47.5
"	80.0	"	51.2

Table 4. Examples of graft copolymerization of acrylic acid onto polypropylene fabric.

Total dose 5.0×10^5 r; Dose rate 3.19×10^4 r/h;
 Fabric/monomer benzene solution *ca.* 1.9 g/20 g;
 Polymerization temperature 60°C.

Pre-irradiation temperature (°C)	Concentration of acrylic acid aqueous solution (%)	Time of polymerization (hr)	% Grafting
10~15	10.0	6.0	18.4
"	20.0	3.0	35.8
"	40.0	"	57.2
"	50.0	"	70.4

and simultaneous irradiation were applied. As PVC fiber has tendency to shrink during graft copolymerization, it was grafted under constant length. The result obtained was shown in Table 5.

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Table 5. Graft copolymerization of acrylic acid onto polyvinyl chloride multifilament yarn.

 Dose rate 3.19×10^4 r/h; Fiber/monomer solution *ca.* 0.6 g/20 g.

Acrylic acid solution		Method*	Irradiation		Polymerization		% Grafting
Concentration (%)	Solvent (wt. ratio)		Total dose (r)	Temperature (°C)	Temperature (°C)	Time (hr)	
30	H ₂ O/Dioxane (50/50)	I	9.5×10^4	<i>ca.</i> 17	—	—	4.0
50	Benzene	II	4.7×10^5	"	60	6.5	9.6
30	"	"	"	"	"	"	16.1
50	H ₂ O/Dioxane (50/50)	"	"	"	"	"	23.6
30	Benzene	I	1.6×10^5	"	—	—	60.5
50	"	"	"	"	—	—	86.3

* I: Simultaneous irradiation in vacuum.

II: Pre-irradiation in the presence of air.

3. Tensile properties

3.1. Acrylic acid grafted PP multifilament yarn

Some tensile properties of acrylic acid grafted and aftertreated PP fiber of multifilament yarn were shown in Table 6. Dry, wet and knot tensile strengths of the fibers were not changed by the graft copolymerization or aftertreatment.

It was noted that any appreciable decrease in wet tenacity of the grafted and Na salt-treated samples was not observed, though relatively large hydrophilic property was given as shown in Table 11 presented below. Relatively high value of Young's modulus in wet state for the sample (about 160 kg/mm²) was

Table 6. Tensile properties of acrylic acid grafted and aftertreated polypropylene fibers.

% Grafting	Control		Na ₂ CO ₃		Ca(CH ₃ COO) ₂		NH ₄ Cl		APO	
	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)
Dry tensile properties										
0	5.83	68.0	—	—	—	—	—	—	—	—
14.8	6.01	77.2	6.31	101.8	6.00	89.1	6.11	142.0	—	—
25.3	6.21	78.3	6.17	78.5	6.35	83.8	5.83	75.1	—	—
26.4	—	—	—	—	—	—	—	—	4.16	53.9
29.5	5.93	102.5	5.53	77.9	6.27	122.5	6.30	95.4	—	—
40.7	5.98	83.5	6.40	89.5	6.24	100.6	6.08	88.3	—	—
Wet tensile properties										
25.3	6.32	88.9	6.09	87.1	5.94	82.1	6.53	80.7	—	—
40.7	5.62	91.2	5.75	100.5	5.55	81.9	5.82	80.5	—	—
Knot tensile properties										
0	6.26	71.3	—	—	—	—	—	—	—	—
25.3	5.91	64.0	5.91	60.2	6.16	56.2	6.41	58.4	—	—
40.7	5.95	70.7	—	—	6.07	75.8	—	—	—	—

* Based on denier of starting yarn.

Table 7. Tensile properties of acrylic acid grafted and aftertreated polypropylene fibers at elevated temperature.

% Grafting	Temperature (°C)	20		100		150		200	
	After-treatment	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)
0	Control	5.83	68.0	3.47	140.9	2.70	148.1	0.58	77.9
25.3	"	6.21	78.7	4.43	119.3	1.93	162.2	1.15	92.0
"	Na ₂ CO ₃	6.17	78.5	3.40	139.8	1.90	135.2	0.67	69.1
"	Ca(CH ₃ COO) ₂	6.35	83.8	3.43	130.8	2.11	125.6	0.69	53.2
"	NH ₄ Cl	5.83	75.1	3.43	120.0	1.84	142.0	1.00	96.5
26.4	APO	4.16	53.9	3.33	109.3	1.96	137.5	0.18	38.4

* Based on denier of starting yarn.

Table 8. Tensile properties of acrylic acid grafted and aftertreated polyvinyl chloride fibers.

% Grafting	Control		Na ₂ CO ₃		Ca(CH ₃ COO) ₂		NH ₄ Cl		APO	
	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)
Dry tensile properties										
0**	2.66	54.6	—	—	—	—	—	—	—	—
16.1	3.73	57.9	2.00	67.1	2.01	84.0	1.93	70.0	—	—
23.6	3.00	51.6	3.25	58.2	3.23	50.3	2.75	74.2	3.01	46.7
Wet tensile properties										
23.6	—	—	2.58	53.8	—	—	—	—	—	—

* Based on denier of starting yarn.

** Original PVC fiber extracted with hot ether.

Table 9. Tensile properties of acrylic acid grafted and aftertreated polyvinyl chloride fibers at elevated temperature.

% Grafting	Temperature (°C)	20		100		150	
	Aftertreatment	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)	Tenacity* (g/d)	Elongation (%)
0**	Control	2.66	54.6	0.73	33.5	0.20	33.3
16.1	Control	3.73	57.9	0.51	77.8	0.18	36.0
"	Na ₂ CO ₃	2.00	67.1	0.58	66.0	0.20	44.1
"	Ca(CH ₃ COO) ₂	2.01	84.0	0.55	67.4	0.18	45.3
"	NH ₄ Cl	1.93	69.8	0.90	52.0	0.14	25.1
23.6	Control	3.00	51.6	1.23	30.8	0.18	12.3
"	Na ₂ CO ₃	3.25	58.2	1.08	19.7	0.18	9.7
"	Ca(CH ₃ COO) ₂	3.23	50.3	1.07	23.1	0.20	8.5
"	NH ₄ Cl	2.75	74.2	1.06	29.5	0.31	13.1
"	APO	3.01	46.7	1.40	31.5	0.48	24.0

* Based on denier of starting yarn.

** Original PVC fibers extracted with hot ether.

obtained by measuring stress-strain curve of 25.3% acrylic acid grafted and Na salt-treated PP fiber.

As low heat shrinkability and high melting temperature of these fibers were obtained as described below, tensile properties at elevated temperature were examined with interest. However, contrary to our expectation, improved tensile properties at high temperature were not obtained as shown in Table 7. These results coincide with that reported by Rogovin *et al.*⁴⁾ indicating grafted side chains did not prevent the tensile decrease of PP main chain caused by elevated temperature.

3.2. Acrylic acid grafted PVC multifilament yarn

Similar results were also observed for PVC fiber as shown in Table 8 and 9.

4. Heat shrinkability and melting temperature

4.1. Acrylic acid grafted PP fiber

The influence of % grafting on the heat shrinkability of the grafted fibers was shown in Fig. 1. Though the maximum shrinkage of PP original fiber was about 37.5% and it broke at 168°C near the melting point of isotactic PP, the maximum heat shrinkage was decreased by acrylic acid grafting. When % grafting became about 62%, the fiber neither showed appreciable shrinkage nor broke till 300°C.

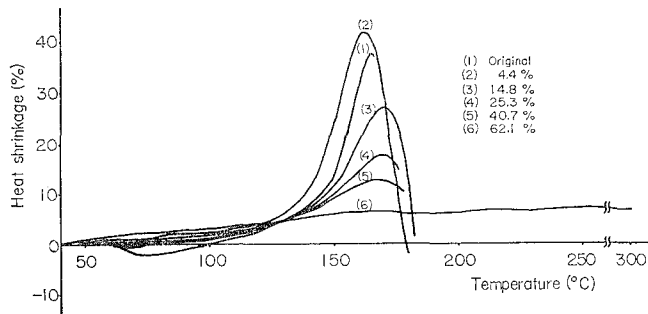


Fig. 1. Heat shrinkage of acrylic acid grafted polypropylene fibers. Grafted percents are shown in figure.

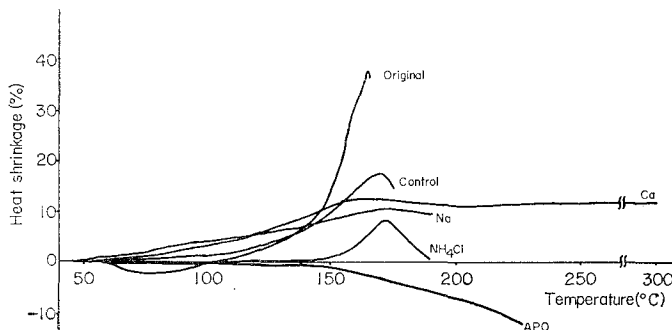


Fig. 2. Heat shrinkage of 25.3% acrylic acid grafted and aftertreated polypropylene fibers.

When about 25% acrylic acid grafted PP fibers were treated with some inorganic metal salts aqueous solutions or curing agents, the heat shrinkage of the treated fibers, especially in the case of Ca salts, was remarkably decreased as shown in Fig. 2.

Though the melting temperature of PP monofilament was scarcely enhanced by acrylic acid grafting alone, remarkable improvement was obtained by Na or

Table 10. Fiber melting temperature of acrylic acid grafted and aftertreated polypropylene monofilaments.

% Grafting	Aftertreatment	Fiber melting temperature (°C)
18.6	Control	185
"	Na ₂ CO ₃	205
"	Ca(CH ₃ COO) ₂	320
33.4	Control	170
"	Na ₂ CO ₃	320
"	Ca(CH ₃ COO) ₂	365

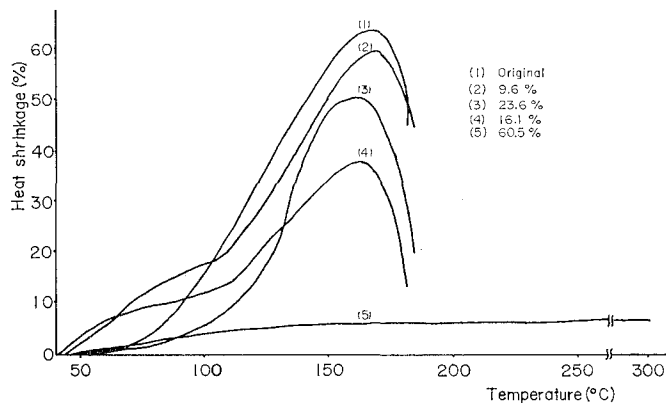


Fig. 3. Heat shrinkage of acrylic acid grafted polyvinyl chloride fibers. Grafted percents are shown in figure.

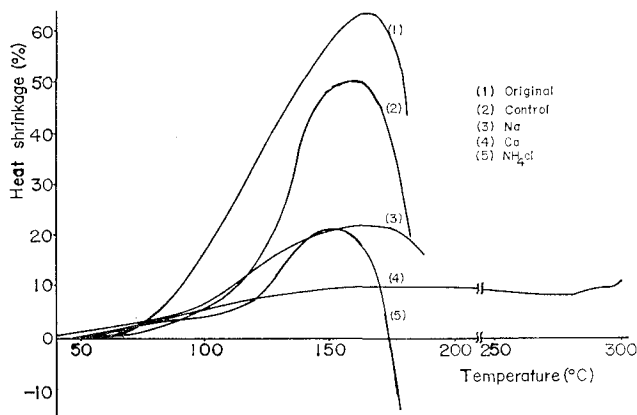


Fig. 4. Heat shrinkage of 23.6% acrylic acid grafted and aftertreated polyvinyl chloride fibers.

Ca salt-treatment after grafting and especially in the case of Ca salt-treatment high melting temperature of above 300°C was observed as shown in Table 10.

4.2. Acrylic acid grafted PVC multifilament yarn

The similar effect as shown in PP fibers was also observed in this case (Fig. 3 and 4).

5. Moisture regain

Moisture regain of PP fabric was increased to some degree by acrylic acid grafting. However, the conversion of the grafted side chains into Na salt resulted remarkable increase as shown in Table 11. Na salt of 35.8% acrylic acid grafted PP fabric indicated above 8% moisture regain. About 25% grafted fabrics with or without Na salt-treatment could be deeply dyed with cationic dyestuff (Deorlene Brilliant Red 3B-Ciba Co.).

Table 11. Moisture regain of acrylic acid grafted and aftertreated polypropylene fabrics.

% Grafting	Aftertreatment	Moisture regain (%)
0	Control	0
3.0	Control	0
	Na ₂ CO ₃	0.7
	Ca(CH ₃ COO) ₂	0.6
18.4	Control	2.0
	Na ₂ CO ₃	3.2
	Ca(CH ₃ COO) ₂	3.1
20.5	Control	1.5
	Na ₂ CO ₃	3.7
	Ca(CH ₃ COO) ₂	2.0
35.8	Control	4.7
	Na ₂ CO ₃	8.4
	Ca(CH ₃ COO) ₂	6.0
57.2	Control	5.9

6. Frictional electricity

By the grafting of such hydrophilic monomer as acrylic acid and further treatment with Na₂CO₃ aqueous solution, hydrophilic property of fabric was enhanced as described above and thus the decrease of the generation of frictional electricity was also expected.

Fig. 5 and 6 show the frictional electricity of PP monofilament and fabric against nylon. The signs of the electric charge were plus for PP and minus for nylon. Though the electricity was decreased to one half of the original PP by acrylic acid grafting alone, the conversion of the grafted side chains into Na salt resulted remarkable decrease in accordance with increasing hydrophilic properties. It was supposed that larger frictional electricity of the grafted samples

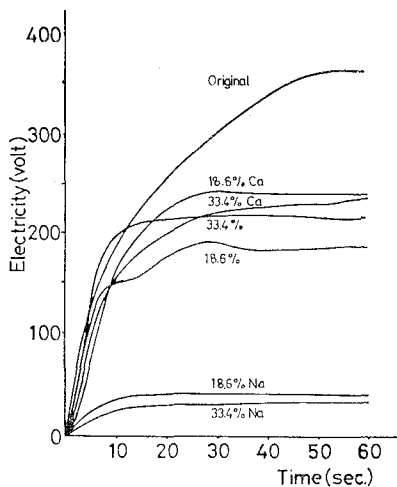


Fig. 5. Frictional static electricity-rubbing time relation of acrylic acid grafted and aftertreated polypropylene monofilaments. Grafted percents are shown in figure.

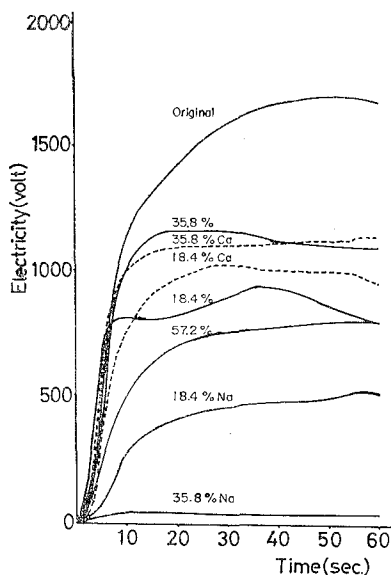


Fig. 6. Frictional static electricity-rubbing time relation of acrylic acid grafted and aftertreated polypropylene fabrics. Grafted percents are shown in figure.

treated with $\text{Ca}(\text{CH}_3\text{COO})_2$ than grafting alone might be related to chemical structural factor including ionic crosslinking, and not always determined by moisture regain alone.

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